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Showcasing Chemical Engineering principles through the production of biodiesel from spent coffee grounds

Sophie Bendall,¹ Max Birdsall-Wilson,¹ Rhodri Jenkins,² Y.M. John Chew^{1*} &

5 Christopher J. Chuck^{1*}

1. Department of Chemical Engineering, University of Bath, Bath, UK, BA2 7AY

2. Doctoral Training Centre in Sustainable Chemical Technologies, Dept. of Chemical Engineering, University of Bath, Bath, UK, BA2 7AY

ABSTRACT

10 Chemical engineering is rarely encountered before higher-level education in the US or in Europe, leaving prospective students unaware of what an applied chemistry or chemical engineering degree entails. In this lab experiment we report the implementation of a 3 day course to showcase chemical engineering principles for 16-17 year olds studying chemistry and mathematics at high school level. The course focused on simple mass
15 and energy balances, reaction engineering and aided the students in making an informed decision towards what to study at university. In addition we introduced sustainability and renewable energy concepts in a laboratory environment.

ABSTRACT GRAPHIC**20 KEYWORDS**

High School / Introductory Chemistry, First-Year Undergraduate / General, Chemical Engineering, Hands-On Learning / Manipulatives, Applications of Chemistry, Fatty Acids, Green Chemistry, Industrial Chemistry, Lipids

25 INTRODUCTION

Due to diminishing crude oil reserves, increasing cost of extraction and a growing awareness of the environmental impact of burning fossil fuels, sustainable alternatives are being increasingly sought. One replacement is biodiesel, the fatty acid alkyl esters produced by transesterification of glycerides, which can be blended with diesel and
30 used for transportation with limited infrastructure change. Currently biodiesel is mainly produced from vegetable oils, such as soybean, rapeseed and palm. These sources have a limited availability and are grown in direct competition with food due to the capacity of cropland needed.¹

As the biodiesel reaction is reasonably simple and the process itself is inherently
35 multidisciplinary, it is an excellent tool to illustrate core chemical, biological and engineering concepts in the laboratory.² For example the synthesis of biodiesel has been the subject of a number of excellent laboratory reports for both high school and undergraduate levels. These include the simple organic synthesis from vegetable oils,³

the conversion of waste cooking oils⁴ and even the cultivation and synthesis from algal
40 lipids.⁵ Similarly a range of biodiesel studies demonstrating the working principles of
common analytical techniques have been published.⁶ Though these techniques mainly
require university equipment, the general properties of biodiesel such as the heat value,
viscosity, Gibbs free energy and discussions on enthalpy and entropy are all applicable
to chemistry high school courses and have been used to demonstrate these concepts.⁷

45 The transesterification of vegetable oils is generally catalysed by bases such as
NaOMe, however, when free fatty acids are present then soap formation can reduce the
yield and make the work-up steps unfeasibly difficult.⁸ On using lower quality
feedstocks in the teaching environment then the transesterification is better catalysed
by a Brønsted acid, such as sulfuric acid, though this does greatly reduce the rate of
50 reaction.⁹

Industrially, the current concern with the manufacture of biodiesel on a large scale
is that 70-95% of the total production cost can be attributed to the cost of the raw
materials. To increase the commercial viability on an industrial scale a relatively low
cost feedstock or waste sources must be implemented.

55 Coffee is one of the world's most widely consumed beverages; in 2013 just under 9
million tonnes of coffee beans were produced worldwide.¹⁰ There are two types of coffee
bean that are grown for commercial use: *Coffea arabica*, more commonly referred to as
Arabica accounts for 75-80% of the world's production and *Coffea canephora*, more
commonly known as Robusta, accounts for 20-25%.¹¹

60 Coffee grounds contain lipid which is predominantly comprised of triglycerides; with
the approximate composition being linoleic acid (44-50%), palmitic acid (35-40%), oleic
acid (7-8%) and stearic acid (7-8%).¹² Coffee oil can be extracted directly from the fresh
coffee grounds (FCG), though on brewing is almost entirely retained in the spent coffee
grounds (SCG). The amount of oil attained from the coffee depends on the source and

65 varies from 11-20 wt % on a dry weight basis.¹³ This oil can then be transesterified to produce biodiesel; assuming that a coffee oil yield of 15 wt % is obtained this could add approximately 340 million gallons of biodiesel to the world's fuel supply per annum.¹⁴

Interestingly while there have been a number of reports in the extraction of oil from coffee,¹²⁻¹⁴ and a few educational papers on the extraction of complex compounds from
70 coffee grounds,¹⁵ to the best of our knowledge there are no papers demonstrating the educational value that this system can be used for. The extraction and conversion of coffee oil to biodiesel is a simple chemistry lab experiment, ideal for use in a high school environment. However, on an industrial scale the choice of extraction conditions, solvents, extraction time, purity of the final product and the methods used will be vital
75 to produce an economic process that ultimately produces a suitable biofuel. Establishing the effectiveness of novel processes lies at the core of chemical engineering. A key metric, especially in the production of fuels, is measuring the conservation of mass and energy in a system.¹⁶ This follows the principal of:

80
$$\text{In} + \text{Generation} = \text{Out} + \text{Consumption} + \text{Accumulation} \text{ (eq.1)}$$

To produce an effective process, then the energy consumption must be minimised and importantly the amount of mass that is not used in the final product must be significantly reduced. In this report a mass balance and energy balance were applied to
85 the production of coffee biodiesel on a laboratory scale to showcase the fundamental tools of the Chemical Engineer.

EXPERIMENTAL OVERVIEW

The laboratory was conducted over 3 days in an introductory course for pre-university high school students who were in the process of applying to university. The
90 course itself was run with 30 students, who were divided into 7 groups. Over the course

of the lab the students were given spent coffee grounds and methods to extract the oil using heptane at room temperature or at reflux. On extraction, the students separated the solvent-oil mixture from the remaining coffee grounds via simple filtration with filter paper or a dead-end membrane flow cell. On removal of the solvent the oil was

transesterified with sulfuric acid and ethanol and the conversion of triglyceride tracked through measurement of the refractive index (RI). Finally the biodiesel was extracted and purified and the resulting purity measured by RI. At each stage the mass of the oil, the coffee grounds and solvents were measured. A spreadsheet and problem sheet (see supporting information) was provided that gave the students all the information required to complete an energy balance and mass balance for the various scenarios that their group undertook.

EXPERIMENTAL DETAILS

Scenarios

Seven scenarios were designed, one per group, so that each group would have different results by the end of the course (table 1).

Table 1. Scenarios designed for the 7 groups of students

Coffee		1	2	3	4	5	6	7
Coffee type		Robusta	Robusta	Robusta	Robusta	Colombian	Colombian	Colombian
Extraction	Solvent	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane
	Temperature (° C)	22	99	99	99	99	22	22
	Number of washes	1	3	2	1	3	2	3
	Time for extraction (min)	60	15	30	60	15	20	15
Separation	Method	Filter paper	Dead-end flow cell	Dead-end flow cell	Dead-end flow cell	Dead-end flow cell	Filter paper	Filter paper
Transesterification	Alcohol-catalyst to oil molar ratio	60 : 1	6:1	6:1	60:1	6:1	60:1	6:1

Materials

Ethanol (laboratory grade) and sulfuric acid (96%) were sourced from Sigma Aldrich Ltd, UK. Heptane (HPLC grade) was obtained from Fisher Ltd, UK. The sulfuric acid was premixed (10 wt% in relation to the oil) with the ethanol prior to the laboratory.

Pre-laboratory set-up

Two types of ground coffee were sourced (Colombian, Arabica beans, and Robusta) from a local retailer. The coffee was chosen carefully to ensure that a minimum of unsaponifiable material was present, which can cause issues in the separation later.

The coffee was then brewed in a French Press coffee maker, the grounds filtered and dried for 24 hours, in accordance with a literature method.¹² The oil was extracted and the RI measured, the coffee was converted into biodiesel by literature methods,¹⁷ purified and the RI calculated. The calibration curves and final purity were calculated according to a standard literature method,¹⁸ based on these values. 20g of purified coffee oil and 10g of purified coffee biodiesel per group were also prepared to allow students to complete the laboratory even if they did not manage to extract or convert the oil. It is also possible to use fresh coffee rather than spent coffee grounds, though fresh coffee will tend to have more unsaponifiable compounds present. The pre-laboratory set-up took two days.

Coffee oil extraction

Coffee oil was extracted from spent coffee grounds using two separate methods, hot and cold extraction. Fifty grams of coffee was weighed out and placed in a round bottom flask (500 ml), 200 ml of heptane was added. A magnetic stirrer was used to aid mixing. Extractions were carried out using a stirrer hotplate. For extractions at room temperature (22 °C), a stopper was added to the flask to reduce evaporative losses. Hot extractions (99 °C) were undertaken using a stirrer hotplate and a reflux condenser over the allotted time. When multiple extractions were needed the coffee was filtered using

filter paper and returned to the round bottom flask with fresh solvent. The resulting coffee grounds were dried overnight and weighed.

135 **Solid-liquid separation**

The coffee grounds were separated from the oil-solvent mixture using a filter paper or a membrane dead-end cell. The time taken for all of the solvent-coffee oil mixture to filter through the filter paper was recorded using a stopwatch. When the filtration had been completed the collection vessel was covered to prevent any solvent evaporating and
140 the wet filter paper containing the SCG was weighed and left to dry, once dried the filter paper was weighed again to determine the amount of solvent that remained in the SCG and filter paper that could not be filtered. The volume of the filtrate was noted so that a volumetric flow rate through the filter paper could be determined.

The membrane used in the pressurised dead-end cell (Millipore amicon stirred cell
145 model 8200 (200 mL), from Cole-Palmer) consisted of inter-woven stainless-steel fibres to create a porous membrane with a nominal pore size of 10 μm . The membrane was cut into a circular shape large enough to cover the bottom of the cell and was fixed into place with a ceramic support. The chamber of the cell was then secured on top of the membrane and the extraction mixture was added. The top of the cell, which was
150 connected to a pressurised air cylinder, was then secured into place and the pressure was set to 1 bar. The time taken for the separation was recorded along with the volume of liquid filtered to give the volumetric flow rate. Once the separation had occurred the wet weight of the filter cake was measured and left to dry, then re-weighed to find the mass of solvent trapped in the SCG.

155 **Solvent recovery**

After the solid-liquid separation, a liquid-liquid separation stage is required to remove the solvent from the coffee oil product. A rotary evaporator was used to achieve the separation. On removal of all the solvent, the resulting oil and flask were weighed, the oil retained and the flask reweighed to give the final mass of oil.

Transesterification reaction

Fifteen grams of coffee oil was transesterified in a two necked flask equipped with reflux condenser. The oil was transferred to the flask and 6 ml ethanol (6:1 molar loading) containing H_2SO_4 (1.5 g) or 60 ml of ethanol (60:1 molar loading) containing H_2SO_4 (1.5 g) was added. The reaction was performed at room temperature (22 °C) and at reflux (79 °C). The kinetics of the reaction was determined by measuring the RI of the oil inside the reaction vessel, this was achieved by sampling at regular intervals of 2, 4 and 6 hours.

Each sample had to be processed to remove any ethanol, catalyst, glycerol and other unwanted chemicals prior to the refractive index being measured. The sample was taken from the reaction vessel and added to 10 ml of heptane, this mixture was then filtered using a 50 ml separating funnel using filter paper to remove any solids that had formed. The mixture was then subjected to three 10 ml washes with brine to remove any unwanted material. After each salt-water wash the mixture was gently shaken and left to separate; the bottom layer was then removed. After the third wash the heptane/oil mixture was collected in a sample vial and the heptane was removed using the rotary evaporator. Once all of the heptane was removed the RI of the sample was taken using a handheld refractometer (DR301-95 KRUESS Digital Handheld Refractometer). To do this, the refractometer was calibrated with deionised water, the sample (~ 0.3 ml) was then added to the viewing chamber, covering the optical lense entirely. The resulting reading was recorded from the digital display.

After 24 hours the reaction products were washed three times with 20 ml of brine to remove the glycerol, ethanol and acid catalyst. The samples were then measured for their RI to assess the purity.

HAZARDS

Ethanol is highly flammable but was chosen for the alcohol used in transesterification as an alternative to methanol as it is less toxic. Sulfuric acid causes

severe burns and was premixed with the ethanol prior to the lab to reduce the exposure of students to glacial acid. Heptane is flammable, can be fatal if swallowed and can cause skin irritation but was used instead of hexane, due to recent concerns over the neurotoxicity of hexane.¹⁹

RESULTS

Each of the 7 groups recorded the mass balance from each of the stages over the three days on flow charts with blanks in to help visualise the mass balance (see supporting information). The energy balance was created by calculating the energy inputs at each stage and filling in the necessary equations in a spreadsheet (table 2, additionally see supporting information for the spreadsheet and the equations used to construct the spreadsheet). The results for all the groups are summarised in table 2. This allowed the students to enter in the steps, and timings and gave them an energy cost for each estimate stage. The RI of pure biodiesel derived from Arabica and Robusta differ slightly and were calculated prior to the laboratory, these values were used to indicate 100% conversion from the triglyceride. The RI showed that by 6 hours, all of the reactions had converted approximately 60% of the triglyceride, though by 24 hours all groups achieved a conversion of over 97.5% (figure 1).

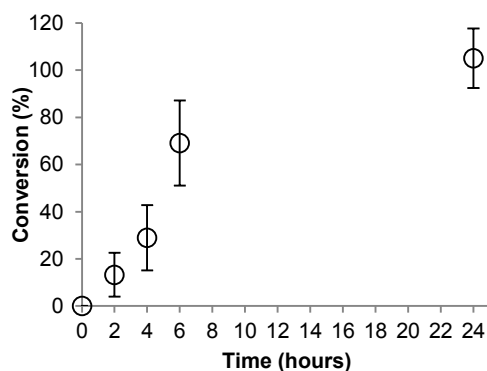


Figure 1. Average conversion of the triglyceride to biodiesel, calculated by using the refractive index. The standard deviation of all the groups results ($n = 7$) is presented as error bars. The RI for the pure Robusta and Arabica biodiesel were calculated prior to the laboratory, this was taken as the measurement for 100% conversion.

Table 2 Energy and mass balance results for the seven groups that completed the laboratory experiment

Group		1	2	3	4	5	6	7
Coffee type		Robusta	Robusta	Robusta	Robusta	Arabica	Arabica	Arabica
Oil Extraction (g)	1	2.71	3.17	3.25	3.33	3.97	3.58	3.65
	2	-	1.42	1.32	-	1.76	1.23	1.12
	3	-	0.37	-	-	0.65	-	0.45
	Total	2.71	4.96	4.57	3.33	6.38	4.81	5.22
Energy used in (MJ)	Extraction	0.06	0.11	0.09	0.06	0.11	0.08	0.11
	Filtration	0	0.01	0.01	0.01	0.01	0	0
	Evaporation	0.11	0.12	0.10	0.13	0.09	0.11	0.12
	Transesterification	0.82	0.78	0.78	0.82	0.78	0.82	0.78
Total energy used (MJ)		0.99	1.02	0.98	1.02	0.99	1.01	1.01
Total energy supplied (MJ)		56.16	55.52	56.09	56.12	55.43	55.29	55.48
Energy lost (MJ)		55.17	54.50	55.11	55.10	54.44	54.28	54.47
Biodiesel yield (mass % from original oil) ^a		81%	95%	94%	100%+	100%+	99%	99%
Energy content of biodiesel (MJ) (* based on 39.65 MJ/kg ⁷)		0.09	0.18	0.17	0.16	0.26	0.19	0.21

^a Some students, presumably due to the incomplete removal of solvent, recorded biodiesel yields of 100% or over. For the energy balance these were assumed to be 100%.

DISCUSSION

210 The laboratory introduces students to the principles of chemical engineering, by applying metrics to an actual chemistry experiment, in this way the importance of engineering in designing processes is highlighted. On completion of the laboratory, the students were asked to present their findings. This was followed by an inclusive group discussion on the results obtained from the cohort as a whole.

215 Firstly, the yield of coffee oil obtained, depending on the source, varies substantially with Robusta giving lower yields (%) than the Colombian Arabica; highlighting the importance of feedstock variation in these processes. We then focussed the students attention on the relative proportions of energy used in each individual stage. For

example, in the extraction multiple washes with fresh solvent were needed to extract the
220 full amount of lipid available with 1 wash only recovering around 60% of the available
lipid, three washes is sufficient to extract most of the lipid. However, the energy used in
extracting the oil was doubled, when using three washes, though hardly any oil was
extracted on the third wash. Problems like these are commonly faced by engineers when
designing a process, as although a higher yield of coffee oil may be obtained by
225 introducing a third wash, it may be too costly for it to be an economically viable option.
The ability to perform an economic analysis and evaluation is an essential skill that
students will develop in the chemical engineering discipline.

Another key factor in extraction is the use of heat. Hot extraction leads to higher
yields as adding heat to the process speeds up the rate of mass transfer. A shorter
230 extraction time is even more beneficial when the hot extraction technique is employed
due to additional energy costs required to heat the solvent. Mass transfer is a key
concept within chemical engineering and discussing factors that affect the rate of mass
transfer is a constructive exercise for the students. When the membrane is used for
filtration a greater yield of coffee oil is recovered. When filtering the SCG with filter
235 paper it is difficult to force all of the solvent/coffee oil liquid through the filter paper and
a small amount is locked in the wet SCG, as such more solvent is recovered using a
membrane. Using a membrane in conjunction with a cold extraction process was seen
to yield more coffee oil than using filter paper after a hot extraction. Interestingly,
though this part of the laboratory takes a long time and the underlying calculations are
240 reasonably complex, the filtration stage had relatively little impact in comparison with
the other methods used. This was generally a surprise to most of the students in the
group, but highlighted the importance of doing these calculations to assess the major
energy inputs.

In terms of energy use however, all of the initial stages have little impact compared
245 to the energy consumption used in the transesterification step, which accounted for
between 78-82% of the total energy of the process. This lead to a discussion on the
merits of reducing the time and temperature in the transesterification stage, and some
of the advances in the area of reaction engineering and design that allows this to be
possible. This observation highlights the need for efficient process control and
250 optimisation on large scale operations.

Another key discussion point, is the efficiency of the energy use in the system.
Depending on the group, the energy used was between 55-56 MJ per experiment with
roughly 98% of that energy being lost to the environment. Reducing energy losses is key
to an effective process, and using this data we were able to discuss the different
255 methods, such as energy recovery or heat integration and co-product processing that
the chemical industry uses to minimise energy loss. Even when only accounting for the
energy that was used for the process, the energy content of the biodiesel produced was
just a fraction (9-28%) of the total energy invested. Obtaining a positive energy balance
is one of the key metrics in determining the sustainability of renewable energy, and a
260 key tool used by engineers in this sector.

Finally the students were challenged on identifying the methods for improved energy
efficiency. This guided discussion led towards concluding that the laboratory glassware
and equipment that they have experience with is not suitable for scaled up reactions in
the chemical industry. Moreover, the case study that we selected introduced the
265 concept of green technology and sustainability. We can also highlight the core aspects
of a chemical engineering course, including mass and heat balances, reaction
engineering, separations and process economics. Throughout this course, students
were also able to explore degree options with university staff and meet peers considering
similar routes.

CONCLUSION

In the lab experiment presented, students considering a chemistry degree were given the tools and an oversight into a more applied, or engineering, style of university degree. Based on student feedback, the students had a much clearer idea of what chemical engineering entails, and how important using the fundamental principles presented are in producing efficient industrial processes. The entire lab experiment was designed to highlight chemical engineering at a university level to high school students, however, aspects of the lab presented, such as the energy and mass balances, could also be used in the classroom where there is no laboratory equipment available. A further strength of this lab experiment is the applied nature of the problem, and the integration of math, chemistry and applied science which fits well with the reforms to math and science syllabuses in the US K-12 system.

ASSOCIATED CONTENT

The student handout, the instructor protocols and the full spreadsheets to calculate the cost, energy and mass balances are available in the supporting information, via the internet at <http://pubs.acs.org>.

AUTHOR INFORMATION**Corresponding Author**

*E-mail: c.chuck@bath.ac.uk, y.m.chew@bath.ac.uk tel: +44(0)1225 383537, fax: +44 (0)1225 386231

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